

# PATENT SPECIFICATION

DRAWINGS ATTACHED



**875,977**

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International Classification:—H01m.

## COMPLETE SPECIFICATION

### Improvements in and relating to Electric Cells.

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State 5 of New York, United States of America, (Assignee of George Raymond Drengler, Milton Bedford Clark, Robert Erskine Stark and Theodore Robert Beatty), do hereby declare the invention, for which we pray 10 that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with anodes 15 and cathodes for batteries, to methods for producing the same and to batteries employing these anodes and cathodes.

New applications demand efficient energy 20 withdrawal from batteries in periods of one to ten minutes in contrast to conventional battery uses in which the service life is measured in days, weeks or months. Equally important, the weight and volume allotment given in these new applications to any 25 component is highly restricted. Thus, electrochemical systems capable of delivering power at high rates are often unusable because of the weight or volume of the systems. Therefore, a continuing effort to 30 toward improving the volumetric and gravimetric efficiency of high rate batteries is being made by battery manufacturers.

The construction practiced by high rate primary battery manufacturers is similar to 35 that used for conventional storage batteries. The battery consists of a number of individual cell compartments contained in a one-piece case. Positioned in each unit cell compartment are an appropriate number 40 of anode and cathode plates together with electrode separators. The total number of plates is dependent upon the desired current output. In the unit cell, all anode plates are connected to a common lead and all 45 cathode plates to a second common lead.

[Pn.

When electrolyte is added, all the plates in one unit cell compartment are immersed in a common solution reservoir. To provide desired battery voltage, several unit cells are electrically connected. This construction 50 method necessitates that each electrode be connected to a current collector of sufficient mass to conduct the current generated to the battery terminals without significant energy dissipation through heat ( $I^2R$ ) losses. This collector is commonly silver-plated copper screen, 0.35 mm. thick and with openings 0.42 mm. square, in applications where the electrode current density is 0.15 55 to 0.23 amperes per sq. cm. The collector in this case represents 35 to 40 per cent of the total electrode weight and volume. Thus, the coulombic capacity per unit weight and volume of the electrodes is at best 60 60 per cent of that obtainable if all the mass were active material. This value is further reduced by the necessity of a multi-compartment case, which adds significant volume and weight to the packaged battery.

The silver oxide-zinc couple in potassium 65 hydroxide electrolyte is the system now most widely accepted for high rate primary batteries. Commercially, the electrodes are electro-formed by multiple charging and discharging of porous silver plates (cathodes) 70 and zinc oxide plates (anodes). This process 75 is slow and costly.

The present invention provides a duplex 80 electrode comprising a thin metallic grid having particles of electro-negative reactive material adhering thereto and a similar grid having particles of electro-positive reactive material adhering thereto, one of said grids being secured to each face of an electronically-conductive, electrochemically-inert separator member.

In the drawings:

Fig. 1 is a series stack arrangement of 85 cells employing the electrodes of the invention;

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Fig. 2 is an exploded view of an electrode in accord with the invention;

Fig. 3 is a cross-sectional view of a mold used in making the electrodes of the invention;

Fig. 4 is the same as Fig. 3, but shows the shim stock grid member positioned on the mold; and

Fig. 5 shows the electrode in the mold under molding pressure.

The electrodes of the invention are formed by compression molding electrochemically-active materials through lightweight, expanded metal grids, and against each face of a thin impervious electronically-conductive, electrochemically-inert cell separator member.

As shown in Fig. 2, the duplex electrode of the invention consists of an electronically-conductive, electrochemically-inert cell separator member 10 which may be 0.025 to 0.075 mm. thick steel shim stock, preferably silver-plated. Lightweight expanded metal grids 12 and 14 serve to hold the active material onto separator 10. The grids may consist of 0.125 mm. thick steel, preferably silver-plated, and expanded to a mesh size having openings 1.5 mm. square.

The duplex electrode of the invention is fabricated as follows:

A grid of silver-plated expanded metal is spot welded to one face of a silver-plated shim stock. The shim stock is made slightly larger in area than the expanded metal to prevent inter-electrode contact. Then oxide depolarizer powder such as divalent silver oxide is compressed through the grid onto the shim at pressures of 700 to 1400 kg./sq. cm. The molding operations for the duplex electrode are illustrated sequentially in Figs. 3 to 5. As shown in Fig. 3, anode or cathode powders are placed in a mold to a depth adjustable to the desired material weight and thickness. Next (Fig. 4), the shim-supported grid is placed over the powder and (Fig. 5) the ram of the molding press is forced against the assembly. A second expanded metal grid then is spot welded to the opposite face of the shim stock, and the other active material is compressed onto it, as described above except that a pressure ranging from 70 to 140 kg./sq. cm. is used.

After molding, the finished electrode (Fig. 1) consists of one anode face 12 (e.g., zinc) and one cathode face 14 (e.g., silver oxide or other oxide depolarizer) supported by an electronically conductive member (shim stock). The grids are visible through the active materials.

To construct a 28 volt unit with silver oxide cathodes and zinc anodes, 18 or 19 of these parts are stacked (with proper regard to polarity), one on top of the other with a suitably sorptive electrode separator

16 (nylon, viscose, vinyon, a copolymer of vinyl chloride and vinyl acetate for example) between the active faces as shown in Fig. 1. The end electrodes in each stack have only one active face with the shim stock serving as a terminal connector.

The grid member in this construction weighs only 0.023 to 0.027 gm./sq. cm., as compared to 0.078 to 0.085 gm./sq. cm. in the best commercial batteries. The duplex construction eliminates the need for a massive conductor, inasmuch as the current path is through the thickness of the stack, and not along the length of the electrodes. This means that in this construction the current path through one electrode is only 0.25 to 0.38 mm., as compared to 38 to 51 mm. in the commercial batteries.

The gravimetric efficiency of the present commercial high rate primary silver cells, exclusive of case and terminals, is 0.066 to 0.077 watt hours per gram. A six cell high rate primary silver cell constructed with the duplex electrodes of this invention provides a gravimetric efficiency of 0.132 to 0.143 watt hours per gram (exclusive of case and terminals). Equally significant, the volumetric efficiency of the construction of this invention is nearly 2.5 times that of the present commercial units (exclusive of case and terminals in each case).

It should be noted that unlike many previous duplex electrodes, those herein described do not require the use of any organic or inorganic binders to achieve adherence of active particles to grid elements.

The duplex electrodes of the invention are particularly suitable for use in reserve-type batteries. In such batteries, a number of electrodes such as depicted on Fig. 1 and 105 on Fig. 2 are positioned in suitable cell containers. Sufficient electrolyte to saturate the electrodes and the bibulous electrode separators is supplied when electricity is desired. It should be pointed out that an 110 amount of electrolyte greatly in excess of that required to saturate the cell elements, such as would occur were the stack to be immersed in electrolyte, will cause inter-cell shorting, and significantly reduce the electrical output. In actual practice, the controlled required amount of electrolyte is added into the stack structure from one or more sides of the stack. The absorption capacity of the separators and electrodes readily removes 120 any accumulation of electrolyte on the exterior of the stack, and thus prevents inter-cell shorting.

The chemically-active particles which may be used in the making of the present duplex 125 electrodes include a large variety of electro-negative and electro-positive reactive materials. Such materials are employed in electrical couples consisting of a metal such as zinc, cadmium, magnesium, lead, iron 130

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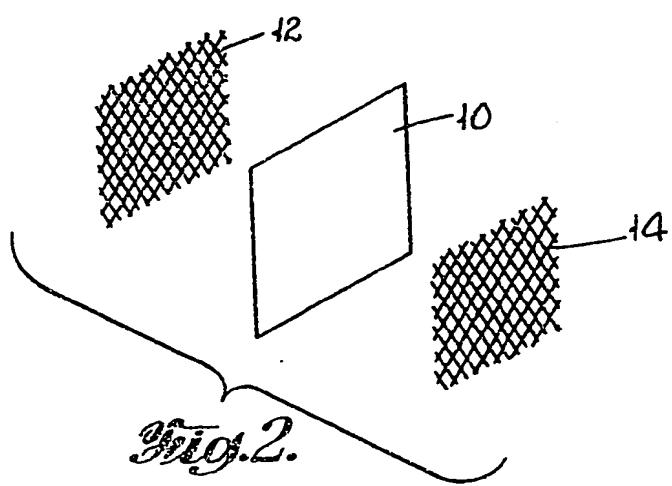
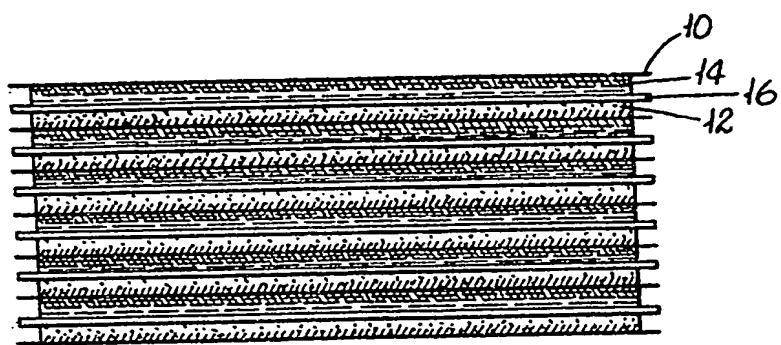
- or aluminium, and an oxide such as silver oxide, mercuric oxide, vanadium pentoxide or manganese dioxide. The amount of the chemically-active materials is determined by 5 the cell thickness desired and the required performance. For a duplex electrode measuring 7.5 by 8.8 cm., a suitable amount of active material on each side is 18 grams.
- The present duplex electrodes can be 10 employed in cells using a variety of electrolytes. Of these, potassium hydroxide solution containing from 31.5 to 33 per cent KOH is preferred.
- WHAT WE CLAIM IS:—
- 15 1. A duplex electrode comprising a thin metallic grid having particles of electro-negative reactive material adhering thereto, and a similar grid having particles of electro-positive reactive material adhering thereto, 20 one of said grids being secured to each face of an electronically-conductive, electrochemically-inert separator member.
2. A duplex electrode as claimed in claim 1, in which the electro-negative reactive 25 material is zinc, cadmium, magnesium, lead, iron or aluminium.
3. A duplex electrode as claimed in claims 1 and 2, in which the electro-positive reactive material is silver oxide, mercuric oxide, 30 vanadium pentoxide or manganese dioxide.
4. A stacked cell construction comprising a container having an electrolyte therein, and at least one duplex electrode as claimed in claims 1, 2 or 3 located in said container.
5. A cell as claimed in claim 4, wherein 35 said electrolyte is an aqueous solution of potassium hydroxide.
6. A method of making duplex electrodes comprising fastening a first thin expanded metal grid to one side of an electronically-conductive, electrochemically-inert separator member, forcing electrochemically-reactive particles through said first grid onto said separator, fastening a second grid on the other side of said separator and forcing electrochemically reactive particles through said second grid onto said separator, said second forcing action being effected at lower pressure than said first forcing action. 40
7. The method of claim 6, wherein said first forcing action is a pressure of 700 to 1400 kg./sq. cm. and said second forcing action is a pressure of 70 to 140 kg./sq. cm. 45
8. Duplex electrodes substantially as hereinbefore described with reference to and as illustrated in Figs. 1 and 2 of the accompanying drawings. 55
9. A cell construction substantially as hereinbefore described with reference to and as illustrated in Fig. 1 of the accompanying drawings. 60
10. A method of making duplex electrodes substantially as hereinbefore described with reference to and as illustrated in Figs. 3 to 5 of the accompanying drawings. 65

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*Fig.1.*

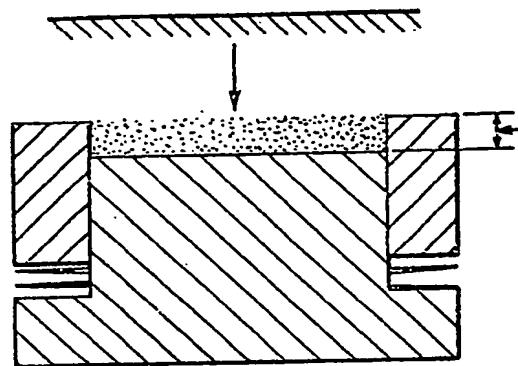


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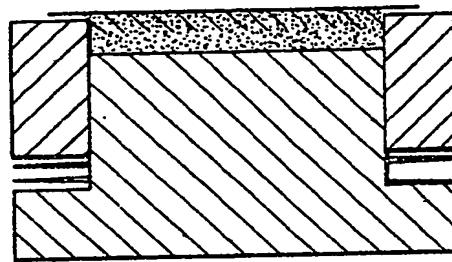
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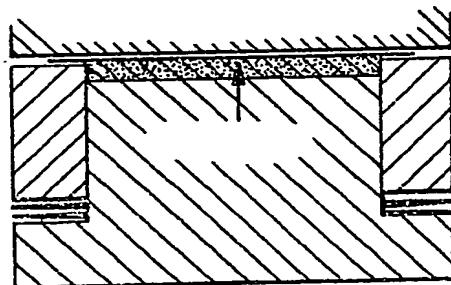
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the Original on a reduced scale.  
SHEETS 1 & 2*



*Fig. 3.*



*Fig. 4.*



*Fig. 5.*

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SHEETS 1 & 2

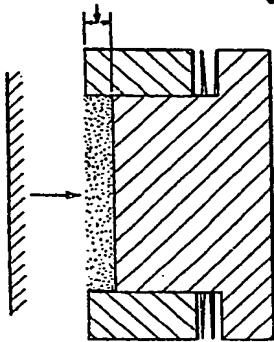


Fig. 1.

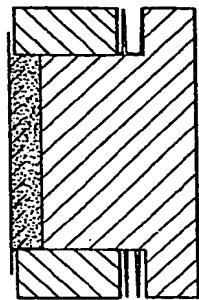


Fig. 3.

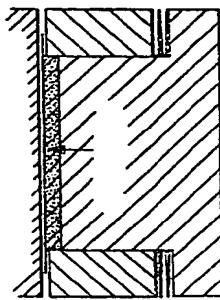


Fig. 5.

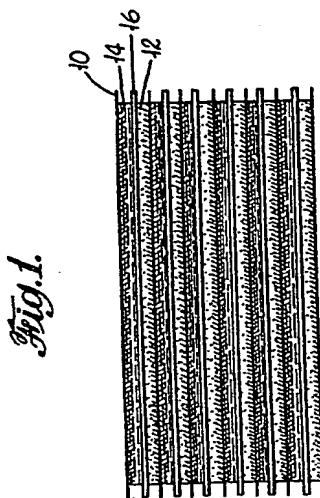


Fig. 1.

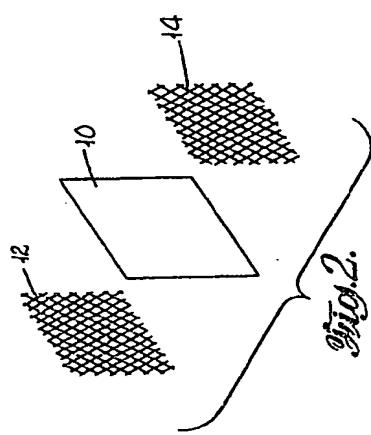


Fig. 2.

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